

Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART XVIII

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In previous publications by the authors, satisfactory values of activation energy (E) and reaction order (n) were calculated from TG data, by means of a computer, using the integrated form of the Arrhenius function. This function was estimated using a truncated asymptotic series or rational approximations (e.g., refs. 1–4). The aim of this paper is to investigate possible expressions for the concurrent evaluation of E and n , which leaves the Arrhenius function intact, but which utilizes an approximate numerical derivative expression to estimate TG slopes. The resulting equations were tested using two sets of theoretical data. A critique of the method is given.

THEORY

For an “ n -order” type unimolecular or pseudounimolecular decomposition by means of TG, we may write the well-known expression [5]

$$RT = (Z/B)\exp(-E/RT)(1 - A)^n \quad (1)$$

where, RT is equivalent to dA/dT , B is constant heating rate, Z is the frequency factor, R is the gas constant, T is temperature (K) and A is the degree of conversion. For values of RT , a numerical approximation was used which involved seven values of A at equally spaced intervals of T . The following derivative approximation used yields values for the central positions and is considered to be the most accurate of similar expressions which yield values at other positions [6],

$$RT(4) = (A_1 - 9A_2 + 45A_3 - 45A_5 + 9A_6 - A_7)/60K \quad (2)$$

where, $RT(4)$ denotes the derivative at A_4 (and T_4) and K is the difference

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in the T -values which are equally spaced. By the use of eqns. (1) and (2), it can be readily shown that

$$\ln(LH) = (-E/R)[K/(KT_1 + T_1^2)] \quad (3)$$

where, $LH = [(1 - A_2)/(1 - A_1)]^n (RT_1/RT_2)$, $(RT_1/RT_2) = (A_1 - 9A_2 + 45A_3 - 45A_5 + 9A_6 - A_7)/(A_2 - 9A_3 + 9A_4 - 45A_6 + 9A_7 - A_8)$. If we now let Y equal the left-hand-side of eqn. (3) and X equal the last term in brackets, then in the expression

$$Y = AA_1 + (AA_2)X \quad (4)$$

$-AA_2$ is equal to E/R and AA_1 should possess a value (theoretical) of zero. By employing successively increasing values of n and a least-squares treatment, values of AA_1 could readily be estimated by computer from TG data [1]. Values of n and AA_2 were considered to be final when the absolute value of AA_1 was closest to zero.

TESTING THE METHOD

The procedure utilized for eqn. (3) is similar to one mentioned previously [1] and will be described only briefly. The initial value of n was taken as 0.100001 and was incremented in steps of 0.1 until the value of AA_1 changed sign. The value of n corresponding to the lower absolute value of AA_1 was then noted (by the computer). A new starting value of n ($n - 0.1$) was then incremented in steps of 0.01 until there again was a change in sign of AA_1 . Final values of n and AA_2 were considered to be those corresponding to the lower absolute value of AA_1 .

The preceding method was tested using theoretical data generated by the authors and from a previous report [7]. In Tables 1 and 2, values of n , slope

TABLE 1

Values of reaction order (N), slope (AA_2) and intercept (AA_1) from theoretical TG data

N	Slope	Intercept
0.10	-77547.5	1.154596
0.20	-61666.8	0.866052
0.30	-45786.0	0.577509
0.40	-29905.3	0.288966
0.50	-14024.6	0.000423
0.60	1856.2	-0.288120
0.50	-14024.6	0.000423
0.51	-12436.5	-0.028431

Final values: $N = 0.50$ and $E = 27.9$ kcal mol⁻¹

TABLE 2

Values of reaction order (N), slope ($AA2$) and intercept ($AA1$) from theoretical TG data [7]

N	Slope	Intercept
0.10	-94828.6	1.753408
0.20	-85973.9	1.558502
0.30	-77119.2	1.363597
0.40	-68264.4	1.168691
0.50	-59409.7	0.973786
0.60	-50555.0	0.778880
0.70	-41700.2	0.583975
0.80	-32845.5	0.389069
0.90	-23990.8	0.194164
1.00	-15136.0	-0.000742
0.90	-23990.8	0.194164
0.91	-23105.3	0.174673
0.92	-22219.8	0.155183
0.93	-21334.3	0.135692
0.94	-20448.9	0.116202
0.95	-19563.4	0.096711
0.96	-18677.9	0.077221
0.97	-17792.5	0.057730
0.98	-16907.0	0.038240
0.99	-16021.5	0.018749
1.00	-15136.0	-0.000742

Final values: $N = 1.00$ and $E = 30.1 \text{ kcal mol}^{-1}$

($AA2$) and intercept ($AA1$) for the theoretical data are depicted. The final results obtained agreed well with the theoretical values. However, it should be noted that the A -values consisted of 6 significant figures (S.F.).

A brief critique of the method follows. Although it is more facile to obtain TG data at various random values of T , the use of equally spaced values of T reduced the complexity of the derivative expression to that in eqn. (2) which is much easier to handle. The method did not involve integration of the Arrhenius function (which cannot be solved in closed form) but instead another approximation was made (for RT) which appears to be less desirable. Due to truncation and rounding errors, it is not generally advisable to use numerical approximations for RT unless the data are changing very smoothly and are measured very accurately. Further, the utilization of the preceding method results in the "loss" of the first three and the last three data points. Because of this, the number of data pairs to be used should well exceed 10. Finally, the number of S.F. for the degree of conversion values can affect final values of E and n based on the testing of the theoretical values in Table 1. In the following, the S.F. and the final values of n and E are given in order (kcal mol^{-1}): 5, 0.50, 27.8; 4, 0.50,

27.6; 3, 0.54, 27.9. Despite the preceding weaknesses, the method may still find use for corroborative and other secondary purposes.

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